

## REMARKS

The claims are 1 to 11.

The above amendment is responsive to points set forth in the Official Action.

With regard to the rejection of claim 3 as indefinite, the preferred embodiments of claim 3 have been deleted and in part inserted in new claim 11.

With regard to the rejection of claim 5 as indefinite, the preferred embodiments have been deleted.

In both claims 3 and 5, the deleted subject matter is encompassed by the broader terminology which remains.

With regard to the rejection of claims 6 and 7 as indefinite, the terminology in issue has been clarified.

Claims 1 to 10 have been rejected under 35 U.S.C 103(a) as being unpatentable over Dupont (U.S. 5,049,623).

This rejection is respectfully traversed.

Dupont relates to compositions comprising ethylenically unsaturated carbamates derived from a styrene allyl alcohol copolymer and an unsaturated isocyanate.

The (meth)acrylated styrene allyl alcohol copolymer is not carbamate. Claim 1 clearly defines the (meth)acrylated styrene allyl alcohol copolymers as those obtained from the (meth)acrylation of a styrene allyl alcohol copolymer with (meth)acrylic acid or with an alkyl(meth)acrylate.

There is no disclosure or suggestion in Dupont on the (meth)acrylated styrene allyl alcohol copolymers according to the invention as presently claimed. One of ordinary skill in the art would not be motivated to replace the ethylenically unsaturated carbamates of Dupont with the (meth)acrylated styrene allyl alcohol copolymer according to the invention as presently claimed.

Hence, the compositions according to claims 1 to 10 are not obvious over Dupont.


With regard to the comment in Official Action paragraph 5, the references not previously considered are submitted herewith and consideration is respectfully requested by initialing them on the PTO-1449 of record.

No further issues remaining, allowance of this application is respectfully requested.

If the Examiner has any comments or proposals for expediting prosecution, please contact undersigned at the telephone number below.

Respectfully submitted,

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**XP-002265686****AN - 1974-89481V [25]****A - [001] 012 02& 034 04- 055 056 109 110 130 133 231 239 27& 341 353 359  
473 48- 656 659****CPY - TOXW****DC - A13 A14 A82 G02****FS - CPI****IC - C08F8/14 ; C09D11/10****MC - A04-C04 A04-F01 A10-E07 A11-C02 A12-W07 G02-A04****PA - (TOXW ) TOYO INK MFG CO****PN - JP49094788 A 19740909 DW197452 000pp****- JP54015707B B 19790616 DW197928 000pp****PR - JP19720117963 19721127****XIC - C08F-008/14 ; C09D-011/10**

**AB - J49094788 Styrene-allyl alc. copolymers (I), acrylic acid or methacrylic acid, and opt. higher fatty acids are esterified to give radically cross-linking hardenable resin compns. useful for vehicles, of u.v. or heat-hardenable printing inks. In an example RJ-100 (I; OH value 300) 495, acrylic acid 105, benzene 80, and hydroquinone 0.6 g were stirred for 19 hr. at 95-97 degrees and the resin (acid value 0.13) obtained was mixed at 90 degrees with 400 g trimethylolpropane triacrylate to give a vehicle. A printing ink prepd. from phthalocyanine Blue-SM 17, the above vehicle 56, benzoine ethyl ether 20, white vaseline 2, trimethylpropanetriacrylate 5, and hydroquinone 0.1 part was dried perfectly when coated (25 mg/100 cm<sup>2</sup>) on an art paper and passed at 50 m/min. under exposure to an u.v. lamp positioned 50-cm apart.**

**IW - RADICAL CROSS LINK HARDEN COMPOSITION PREPARATION STYRENE ALLYL ALC COPOLYMER METHO ACRYLIC ACID**

**IKW - RADICAL CROSS LINK HARDEN COMPOSITION PREPARATION STYRENE ALLYL ALC COPOLYMER METHO ACRYLIC ACID**

**NC - 001****OPD - 1972-11-27****ORD - 1974-09-09****PAW - (TOXW ) TOYO INK MFG CO**

**TI - Radically cross-linking hardenable compsns. - prepd. by esterificn. of styrene allyl alc. copolymers and (meth)acrylic acid**

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## Photoinitiator-freie UV-Härtung von Acrylaten

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Die Initiierung der radikalischen Photopolymerisation von Acrylaten erfolgt in der Regel durch den Zusatz von Photoinitiatoren zur Formulierung. Bei Bestrahlung mit UV-Licht werden die initiierenden Spezies (Radikale) durch photolytische Spaltung des Photoinitiators gebildet. Photoinitiatoren ermöglichen erst die hohe Effizienz der UV-Härtung, da eine direkte Anregung der reaktiven Gruppen im Acrylat aufgrund der geringen Photonenenergie der üblicherweise verwendeten Strahlungsquellen (Quecksilberdampflampen, XeCl-Excimer-Strahler) nicht möglich ist. In der vernetzten Schicht wirken sich jedoch unumgesetzte Reste und Spaltprodukte des Photoinitiators negativ auf die Produkteigenschaften aus (Vergilbung, Geruch, Migration u.a.). Außerdem tragen Photoinitiatoren meist in erheblichem Umfang zu den Gesamtkosten der Beschichtung bei. Ein Verzicht auf den Photoinitiator oder zumindest eine Verringerung der notwendigen Konzentration wäre daher aus Sicht der Anwendung wünschenswert.

Im Rahmen eines Projektes wurde untersucht, ob durch Bestrahlung mit kurzwelligem UV-Licht eine direkte Anregung der Doppelbindungen im Acrylat möglich ist. Mit der Einführung des KrCl-Excimer-Strahlers steht dazu nun eine UV-Quelle mit einer intensiven kurzwelligen Emission bei 222 nm zur Verfügung. UV-Licht mit einer Wellenlänge unterhalb von ca. 240 nm wird von Acrylaten - wie von den meisten organischen Verbindungen - absorbiert. Die Extinktionskoeffizienten hängen dabei in erheblichem Umfang von der chemischen Struktur der Acrylate ab.

Durch Grundlagenuntersuchungen mittels Real-Time-FTIR-Spektroskopie konnte gezeigt werden, dass durch Bestrahlung dünner Acrylatschichten (4,5 µm) mit 222 nm ausreichend Radikale gebildet werden, um eine Photopolymerisation zu initiieren (Abb. 1). Notwendig ist dabei allerdings eine sorg-

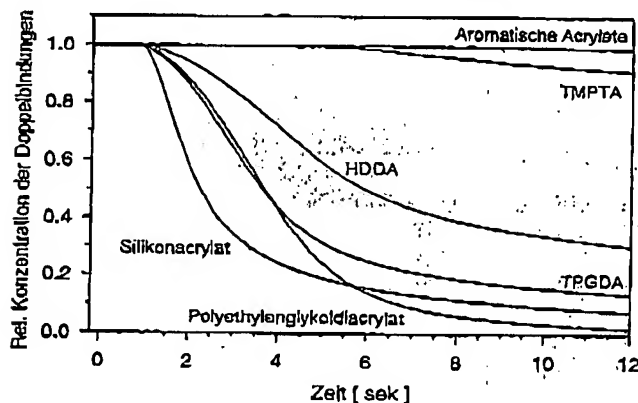


Abb. 1: Kinetik der photoinitiatorfreien UV-Härtung verschiedener Acrylate bei Bestrahlung mit 222 nm.

①

fältige Inertisierung, um die Inhibierung der Reaktion durch Sauerstoff zu unterdrücken. Aromatische Acrylate vernetzen nur in sehr dünnen Schichten (unter 1 µm), da die anregende Strahlung aufgrund der hohen Extinktionskoeffizienten nahezu vollständig in einer dünnen Oberflächenschicht absorbiert wird. Dagegen können aliphatische Acrylate in Schichtdicken von einigen Mikrometern vernetzt werden /1/.

Um Aufschluss über einen möglichen Initiierungsmechanismus zu erhalten, wurden die bei der Bestrahlung von Acrylaten mit kurzwelligem UV-Licht erzeugten Spezies mit Hilfe der Laserphotolyse untersucht. Abb. 2 zeigt am Beispiel von TMPTA typische Absorptionsspektren von Transienten, die nach der Bestrahlung eines Acrylates mit einem Laserimpuls beobachtet werden.

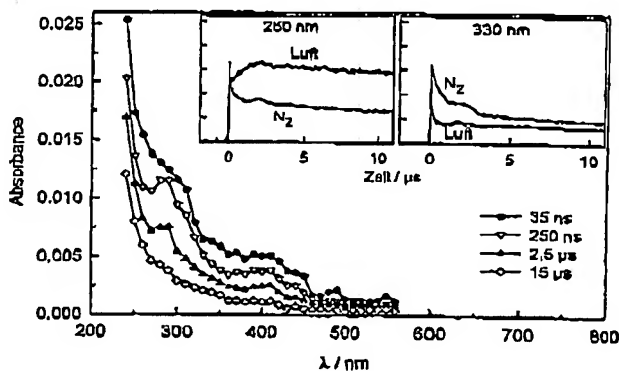


Abb. 2: Transientenspektren von TMPTA in Acetonitril (N<sub>2</sub>-gesättigte Lösung) nach Laserphotolyse mit 222 nm. Im Inset: zeitlicher Verlauf bei verschiedenen Wellenlängen in Abhängigkeit von der Begasung.

Mit Hilfe begleitender quantenchemischer Berechnungen zur Interpretation der mit Laserphotolyse erhaltenen Resultate konnte gezeigt werden /1/, dass sich innerhalb von 200 ns zunächst ein stark lokalisierter Triplett-Zustand an der C=C-Doppelbindung bildet. Durch inter- bzw. intramolekularen H-Transfer oder Addition an die Doppelbindung eines weiteren Acrylatmoleküls erfolgt daraus nach ca. 3 µs die Bildung von Radikalen bzw. Biradikalen, die im weiteren Verlauf die Polymerisationsreaktion initiieren. Aus energetischer Sicht wird dabei die Biradikalbildung begünstigt.

Durch Bestrahlung dünner Acrylatschichten (2 µm) mit einem KrCl-Excimer-Strahler an einer Technikanlage des IOM konnte ferner demonstriert werden /1/, dass Acrylate auch ohne zugesetzten Photoinitiator unter inerten Bedingungen bei Bahngeschwindigkeiten bis etwa 30 m/min vernetzt werden können. Es wird erwartet, dass eine noch raschere Reaktion möglich ist, sobald leistungsstärkere Excimerstrahler zur Verfügung stehen.

/1/ T. Scherzer, W. Knolle, S. Naumov, R. Mehnert, *UV curing without photoinitiators*, Proc. RadTech Europe 2001 Conference, Basel, 8.-10.10.2001, pp. 225-231.

XP-002265685



# SARTOMER APPLICATION BULLETIN

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## Non Irritation Acrylates For UV/EB Curing

### Abstract

One of the most important barriers to the development of the acrylate-based UV and EB cure technology has traditionally been the toxicity, or moreover, the skin and eye irritation of acrylate oligomers and monomers. This problem has been effectively addressed by the development of a range of non-skin and eye irritant acrylate oligomers, oligoetheracrylates and oligoacrylates. This paper familiarizes you with these new user-friendly products and shows you how to formulate UV and EB curing inks, coatings or adhesives while avoiding the Risk-Phrase R38 (Irritating to Skin) or St. Andrew's cross (Xi, irritant) altogether on the label in European countries.

It is important to realize that the classification and label relate to hazard and not risk. Hazard is the intrinsic property of a substance, whereas risk relates to whether the hazard will occur, taking into account how the substance will be handled. Using the correct gloves, as detailed in the safety data sheet, will ensure that the hazard is correctly controlled.

### Introduction

In the early days of radiation curing, it was discovered that some monomers or reactive diluents have irritant properties. This sometimes resulted in severe skin and eye irritation for workers, especially printers, working with these materials. As a result, the labelling of these products (see Table I in the next section) was regulated at the EEC-level in Annex I<sup>1</sup>. In the UK, the use of these products was excluded from use in printing inks and varnishes according to a recommendation of the Society of British Printing Ink Manufacturers and they were listed in a so-called exclusion list<sup>2</sup>.

Skin and eye irritation at this time was expressed in

terms of the Draize test<sup>3</sup>. The Draize skin irritation test is a particularly severe test in that the product to be tested is applied to two sites on the skin of the test animal (rabbit) one of which is abraded.

Since then, several improvements in acrylate monomer production have been implemented. Toxic solvents like benzene were removed from the production process. In addition, product purity was significantly improved resulting in diminished low molecular weight by-products. Last but not least, the level of residual acrylic acid and residual solvents was dramatically reduced.

At least as important as these product improvements was the fact that the raw material suppliers to the UV- and EB-curing industry reacted to the alarming discovery of severe skin and eye irritation of the first generation acrylate monomers with the development of intrinsically low irritancy products. This led to the development of monomers such as GPTA (SR-9020), that were only mildly irritating in the DRAIZE skin-irritation test. As a result replaced monomers like 1,6-hexanediol diacrylate (SR-238), triethylene glycol diacrylate (SR-306), trimethylolpropane triacrylate (SR-351), pentaerythritol triacrylate (SR-444) and pentaerythritol tetraacrylate (SR-295) in many applications, especially in printing inks and overprint varnishes (in line and off line).

On the EEC-level, the DRAIZE tests were replaced by the so-called OECD tests<sup>4,5</sup> for reasons of international harmonization and animal care. The OECD skin-irritation test uses only three instead of six animals and the product to be tested is only applied on the intact, non-abraded skin of the test animals. Because of this, the OECD skin irritation test is considered to be a more relevant test than the DRAIZE test.

Further product improvements and new product developments, which are still ongoing, have resulted in less irritant products becoming available. The third gen-

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eration of acrylate monomers was developed comprising oligoetheracrylates like propoxylated neopentyl glycol diacrylate (SR-9003) and oligoacrylates like ditrimethylolpropane tetraacrylate (SR-355) and dipentaerythritol pentaacrylate (SR-399).

Advances in oligomer acrylate production led to the development of epoxy acrylates with low residual acrylic acid and low residual epoxy values and urethane acrylates with low residual hydroxyacrylate and low isocyanate values. In addition, the low to very low viscosity amine modified polyether acrylates were developed.

Based on animal testing of these products according to the OECD protocols, many of these products do not require labelling as irritants.

#### Products

According to Annex I to the dangerous substance directive and its amendments<sup>6,7</sup> some acrylate monomers require special labelling (see Table I). Generally this is because these monomers are either skin-sensitizers, toxic or corrosive. It is important to realize, though, that these monomers are exceptions, as to their toxicological properties, compared to the wide variety of acrylate monomers and oligomers available.

**TABLE I**

Product	Symbol	Risk phrases	Category
1,6-Hexanediol diacrylate	Xi	R36/38+43	I
Pentaerythritol triacrylate	Xi	R36/38+43	I
Pentaerythritol tetraacrylate	Xi	R36/38+43	I
Triethylene glycol diacrylate	Xi	R36/38+43	I
Trimethylolpropane triacrylate	Xi	R36/38+43	I
Tripropylene glycol diacrylate	Xi	R36/37/38+43	I
1,3-Butylene glycol diacrylate	C	R21+34+43	II
1,4-Butanediol diacrylate	C	R21+34+43	II
Diethylene glycol diacrylate	T	R24+36/38+43	IIIa
Neopentyl glycol diacrylate	T	R24+36/38+43	IIIb

#### DANGER SYMBOLS AND RISK PHRASES

Xi	irritant
Xn	harmful
C	corrosive
R21	harmful in contact with skin
R34	causes burns
R36	irritant to the eyes
R37	irritating to respiratory system
R38	irritant to skin
R36/38	irritant to the skin and eyes
R41	risk of serious damage to eyes
R43	may cause skin sensitization

Apart from the specific labelling requirements for these monomers according to Annex I, the labelling of prepa-

rations (mixtures of substances) containing these monomers is strictly regulated in Annex I.

Table II presents a summary of the labelling of a formulation according to the amount and nature of the components. The most frequent cases are encountered with acrylates labelled Xi, R36/38, or even in the case of TPGDA, Xi, R36/37/38+R43. S represents the total amount of labelled products.

We can give the following examples :

Formulations containing irritant components (all remaining products are assumed to be non-irritant):

- 1 % TPGDA (R36/37/38+43) ;
- 8 % EOEOEA (R21/38/41/43) ;
- 10 % THFA (R36/38) ;
- 10 % ethoxylated<sub>20</sub> TMPTA (R36/38) ;
- 10 % THFA + 10 % ethoxylated TMPTA ;

formulation : Xi, R43  
 formulation : Xi, R36/43  
 formulation : no labelling  
 formulation : no labelling  
 formulation : Xi, R36/38

These five examples illustrate the complexity of labelling UV-curable compositions. On the other hand, it is possible to improve a non-Xi formulation through a small amount of an Xi product, provided the total amount of Xi products remains below 20%. Specialty monomers such as IBOA (SR-506), for adhesion to plastics, PEG 600 DA (SR-610), for water compatibility and flexibility, or metallic diacrylates

(SR-9016), for adhesion to metal and higher levels of matting, can in some cases be incorporated at levels up to 20 % without altering the labelling. The most problematic case is the use of sensitizing products, where a percentage as low as 1 leads to a Xi, R43 labelling. The three columns on the right in Table II represent the most frequent cases encountered in UV coatings, inks and adhesives.

TABLE II

Labelling of the components	Xn R20 R21 R22	T R23 R24 R25	C R34	Xi R36 R37	Xi R41	Xi R43
Amount of the labelled components						
$0 \leq S < 1$	-	-	-	-	-	Xi R43
$1 \leq S < 3$	-	Xn R23 R24 R25	Xi R36 R38	-	-	Xi R43
$3 \leq S < 5$	-	Xn R23 R24 R25	Xi R36 R38	-	Xi R36	Xi R43
$5 \leq S < 10$	-	Xn R23 R24 R25	C R34	-	Xi R41	Xi R43
$20 \leq S < 25$	-	Xn R23 R24 R25	C R34	Xi R36 R37 R38	Xi R41	Xi R43
$25 \leq S$	Xn R20 R21 R22	T R23 R24 R25	C R34	Xi R36 R37 R38	Xi R41	Xi R43

### Non Irritant Products

The following products do not generally require labeling with Xi or any other danger symbol, or the risk-phrases R36 and R38 or any other risk phrases based

on animal testing according to the OECD-protocols 404<sup>4</sup> and 405<sup>5</sup> and in compliance with the regulations of Annex IV of the dangerous substance directive<sup>8</sup>.

**TABLE III**

Designation	Chemical name or description
CN-104	bisphenol A epoxy acrylate oligomer
CN-104I80*	bisphenol A epoxy acrylate oligomer, 80% in NPGPODA
CN-115	low viscosity modified bisphenol A epoxy acrylate oligomer
CN-116	fatty acid modified epoxy acrylate
CN-190*	modified tetrafunctional epoxy acrylate
CN-435**	water thinnable polyether acrylate oligomer
CN-501	amine modified polyether acrylate oligomer
CN-704	acrylated polyester adhesion promoter
CN-925*	modified aliphatic urethane tetraacrylate
CN-934	aliphatic polyether urethane acrylate oligomer
CN-965	aliphatic polyester urethane acrylate oligomer
SarCat® K126	cycloaliphatic epoxy oligomer
SR-339	2-phenoxyethyl acrylate
SR-349	ethoxylated bisphenol A diacrylate
SR-355	ditrimethylolpropane tetraacrylate (diTMPTTA)
SR-399	dipentaerythritol pentaacrylate (diPePA)
SR-530*	trimethacrylate ester
SR-9003	propoxylated neopentyl glycol diacrylate (NPGPODA)
SR-9021	highly propoxylated glycerol triacrylate

\* not available in the US

\*\* available in the US as SR-9035

Although these products do not require labelling, it is recommended to avoid contact with skin and eyes when using either these products or formulations containing them.

**CN-104** is a bisphenol A epoxy acrylate, supplied as 100% oligomer. It presents a high reactivity and an excellent flow. The cured film exhibits high hardness and gloss.

**CN-104I80** is **CN104** bisphenol A epoxy acrylate, supplied at 80% oligomer in propoxylated neopentyl glycol diacrylate (**SR-9003**). In addition to the property advantages of **CN-104**, this product has excellent substrate wetting.

**CN-115** is a modified aromatic epoxy acrylate, supplied at 100% oligomer. It has a low viscosity and chemical resistance and is highly reactive.

**CN-116** is a modified epoxy acrylate oligomer. Fast cure response, flexibility, and chemical resistance make **CN-116** a suitable choice for topcoats and sealers for paper, wood, and metal coatings. **CN-116** is particularly suited to lithographic ink applications due to its enhanced hydrophobic character relative to standard bisphenol A epoxy acrylates.

**CN-435** is a low viscosity, trifunctional polyether acrylate. This product is water thinnable and yields clear solutions up to water addition levels of 50%. This



product can also be used as a compatibilizer for other products: blending another into CN-435 makes the resulting blend water thinnable. In the US this product is designated SR-9035.

CN-501 is a very low viscosity, highly reactive amine modified polyether acrylate. Along with a high chemical resistance, it exhibits very low yellowing, comparable to that of an aliphatic urethane acrylate, because of its unique stabilizer package.

CN-704 is an acrylated polyester adhesion promoter that provides excellent adhesion to polyolefins, such as polyethylene and polypropylene. CN-704 is designed for UV/EB cured inks and coatings. Due to its low acid value, CN-704 can be used in formulations containing tertiary amines. Usage levels of 40% to 60% are recommended.

CN-934 is a low viscosity aliphatic urethane acrylate, supplied as 100% oligomer showing good flexibility and adhesion properties.

CN-965 is an aliphatic polyester urethane acrylate, supplied as 100% oligomer with very high flexibility, toughness and adhesion.

SarCat® K126 is a cycloaliphatic diepoxide monomer which serves as the primary reactive component in cationic UV curable coating systems and inks.

SR-339, 2-phenoxyethyl acrylate, is a very low viscosity monofunctional acrylate monomer with high flexibility, excellent solvency and good adhesion on plastic substrates.

SR-349, ethoxylated bisphenol A acrylate, has good scratch resistance and good pigment wetting.

SR-355, ditrimethylolpropane tetraacrylate, gives high reactivity and good chemical and scratch resistance.

SR-399, dipentaerythritol pentaacrylate, is typically used at levels below 10% to significantly increase cure speed, chemical resistance and scratch resistance.

SR-9003, propoxylated neopentyl glycol diacrylate, is a versatile difunctional reactive diluent with low surface tension, good pigment wetting and low shrinkage

resulting in good adhesion to non-porous substrates. In flexibility and hardness it is very similar to HDDA. In solvency and reactivity it is similar to TPGDA.

SR-9021, highly propoxylated glycerol triacrylate, is a versatile trifunctional oligoether acrylate with properties very similar to GPTA which makes it an excellent choice for lithographic inks and varnishes. It is slightly more flexible than GPTA.

### Labelling Requirements

In the EC, the formulations are to be classified and labelled according to the criteria laid down in the dangerous substance directive<sup>9</sup>. This implies that the classification and labelling of the various components of the preparation are known, either because they are listed in Annex I of the council directive 67/548/EEC (see Table I and the comments in the section entitled *Products*), or because they have been evaluated according to the criteria laid down in Annex VI of the same directive.

Should the classification and labelling of all components not be known, the preparation could be regarded as a substance and evaluated by means of the criteria laid down in council directive 67/548/EEC and in particular in Annex VI.

There might be some confusion as to the labelling requirements for acrylates other than those mentioned in Annex I. There is a generic heading for acrylates in Annex I, which in essence covers monofunctional acrylate esters with a simple alkyl radical only. This means a formulation containing components not requiring labelling with a danger symbol or risk phrases and equal to or greater than 10% of a monofunctional acrylate monomer with a simple alkyl radical (see Table IV for the most common examples) requires labelling with Xi and the risk phrase R36/37/38. Below 10%, no labelling is required.

Formulations containing all other acrylate monomers, i.e. all except those mentioned in Table I and V, comply with rules of the dangerous preparations directive.

### Experimental

Testing of the resistance to household chemicals was

**TABLE IV**

**Products**  
 isooctyl acrylate  
 n-octyl acrylate  
 octyl/decyl acrylate  
 isodecyl acrylate  
 lauryl acrylate  
 stearyl acrylate  
 tridecyl acrylate

carried out in compliance with the ISO standard 4211<sup>10</sup>. All household chemical resistances were measured on 12m films on white cardboard, cured at a

speed of 16 m/min with one standard mercury arc lamp (120 W/cm). Adhesion to PVC was evaluated in a cross hatch test using adhesive tape with the indicated adhesive force.

### Results and Discussion

In this section, formulations that do not require labelling with a danger symbol or risk phrases are compared to formulations that do require labelling with a danger symbol and risk phrases (at equal viscosity) in terms of products used and performance.

### Formulation I : Low gloss, low viscosity UV curable topcoat for wood furniture

Does not require labelling with a danger symbol or risk phrases

		<u>%</u>
CN-501 <sup>a</sup>	amine modified polyether acrylate	83.5
SR-489 <sup>a</sup>	tridecyl acrylate	0.5
CN385 <sup>a</sup>	benzophenone	3
Irgacure 184 <sup>b</sup>	photoinitiator	1
Orgasol 3501 EXD Nat 1 <sup>c</sup>	polyamide matting agent	10
Lanco Wax PP1340F <sup>d</sup>	polypropylene wax	2

Viscosity (DIN Cup #4 @25°C)	41 sec
Gloss (60 (12m, 16 m/min)	22%
Reactivity (1 lamp, 120W/cm)	16 m/min
Acetone resistance @25 m/min	30 sec
Acetone resistance @30 m/min	16 sec
Coffee resistance	very slightly marked
Tea resistance	OK
Water resistance	OK

Formulation I has been developed for vacuum application on wood for furniture applications. The objective was to develop a low gloss, low viscosity formulation with high reactivity that does not require labelling with Xi or risk phrases. In this particular case, it was impossible to develop a formulation with the same performance but requiring labelling with a danger symbol and safety phrases, clearly showing that non-irri-

tant products sometimes have unique properties that cannot be matched by products that do require labelling. The amine modified polyether acrylate is used as the base oligomer for its low viscosity and high reactivity. Tridecyl acrylate is added to overcome foaming problems by introducing a low degree of incompatibility of the non polar tridecyl acrylate and the highly polar amine modified polyether acrylate. As you can

see, the resistance to household chemicals is very good indeed: only coffee stained very slightly. The coffee

stain test was found in our studies to be one of the most severe tests.

## Formulation II : Low gloss medium viscosity UV-topcoat for wood furniture

IIa : does not require labelling with a danger symbol or risk phrases

		%
CN-501 <sup>a</sup>	amine modified polyether acrylate	70
CN-104 <sup>a</sup>	bisphenol A epoxy acrylate	16
CN-385 <sup>a</sup>	benzophenone	4
Irgacure 184 <sup>a</sup>	photoinitiator	2
Syloid ED80 <sup>d</sup>	silica matting agent	8

Viscosity @25°C	510 mPa.s
Gloss (60°)	50%
Reactivity (1 lamp, 120W/cm)	50 m/min
Acetone resistance @30 m/min	>60 sec
Acetone resistance @40 m/min	38 sec
Acetone resistance @50 m/min	27 sec
Coffee resistance	did not mark
Tea resistance	did not mark
Water resistance	did not mark

IIb : does require labelling with Xi+R36/38+43

		%
CN104D80 <sup>a</sup>	epoxy acrylate, 80% in GPTA	37
SR-454 <sup>a</sup>	ethoxylated trimethylopropane triacrylate (TMPEOTA)	15
SR-238 <sup>a</sup>	1,6-hexanediol diacrylate (HDDA)	27
CN385 <sup>a</sup>	benzophenone	4
CN386 <sup>a</sup>	acrylated amine synergist	7
Syloid ED 80 <sup>d</sup>	silica matting agent	8
Irgacure 184 <sup>b</sup>		2

Viscosity @25°C	520 mPa.s
Gloss (60°)	48%
Reactivity (1 lamp, 120W/cm)	50 m/min
Acetone resistance @30 m/min	>60 sec
Acetone resistance @40 m/min	60 sec
Acetone resistance @50 m/min	30 sec
Coffee resistance	did not mark
Tea resistance	did not mark
Water resistance	did not mark

Formulations II were developed for roller application on wood for furniture. Because the viscosity requirement is much higher than for Formulation I, a classical silica matting agent could be used. The reactivities of Formulations IIa and IIb are very similar. The acetone resistance of Formulation IIb is slightly better, probably because of the higher degree of crosslinking of the latter. This is achieved by using a relatively high amount of crosslinking oligoether acrylates like propoxylated glycerol triacrylate (SR-9020) and ethoxylated trimethylolpropane triacrylate (SR-454). The same acetone resistance could be achieved for

Formulation IIa by using ditrimethylpropane tetraacrylate (SR-355) or dipentaerythritol pentaacrylate (SR-399). These two products would not affect the labelling of formulation IIa, regardless of the addition level, as they do not require labelling with a danger symbol or risk phrases.

As to the resistance to household chemicals, both formulations gave excellent results with no marking evident even when subjected to the severe coffee stain test.

### Formulation III : High gloss UV-curable topcoat for furniture

IIIa : does not require a danger symbol or risk phrases

		%
CN-104I80 <sup>a</sup>	bisphenol epoxy acrylate, 80% in NPGPODA	45
SR-9003 <sup>a</sup>	propoxylated neopentyl glycol diacrylate (NPGPODA)	35.1
SR-399 <sup>a</sup>	dipentaerythritol pentaacrylate (diPePA)	4
CN-385 <sup>a</sup>	benzophenone	4
CN-386 <sup>a</sup>	acrylated amine synergist	9.9
Irgacure 184 <sup>b</sup>	photoinitiator	2

Viscosity @25°C	400 mPa.s
Reactivity (1 lamp 120W/cm)	45 m/min
Acetone resistance @15 m/min	6
Acetone resistance @45 m/min	3
Coffee resistance	very slightly marked
Tea resistance	did not mark
Water resistance	did not mark

IIIb : does require labelling with Xi and R36/37/38+43

		%
CN-104A80 <sup>a</sup>	bisphenol A epoxy acrylate, 80% in TPGDA	46
SR-306 <sup>a</sup>	tripropylene glycol diacrylate (TPGDA)	28
SR-9020 <sup>a</sup>	propoxylated glycerol triacrylate (GPTA)	10
CN-385 <sup>a</sup>	benzophenone	4
CN-386 <sup>a</sup>	acrylated amine synergist	9.9
Irgacure 184 <sup>b</sup>	photoinitiator	2

Viscosity @25°C	410 mPa.s
Reactivity (1 lamp 120W/cm)	45 m/min
Acetone resistance @15 m/min	6
Acetone resistance @45 m/min	4
Coffee resistance	very slightly marked
Tea resistance	did not mark
Water resistance	did not mark

Formulations III were developed for roller application on wood for furniture. Here again, the reactivity, acetone resistance and resistance for household chemicals were identical for the formulation that does not require labelling with a danger symbol or risk phrases and the one that

does require such labelling. As you can see, only 4% of dipentaerythritol pentaacrylate (SR-399) was necessary to give the same reactivity and chemical resistance as 10% propoxylated glycerol triacrylate (SR-9020).

#### Formulation IV : Non penetrating UV-varnish for paper

IVa : does not require a danger symbol or risk phrases

		<u>%</u>
CN104I80 <sup>a</sup>	bisphenol A epoxy acrylate, 80% in NPGPODA	44
SR-9003 <sup>a</sup>	propoxylated neopentyl glycol diacrylate (NPGPODA)	30.9
SR-355 <sup>a</sup>	ditrimethylolpropane tetraacrylate (diTMPTTA)	3.2
CN385 <sup>a</sup>	benzophenone	6
CN386 <sup>a</sup>	acrylated amine synergist	9.9
Irgacure 184 <sup>b</sup>	photoinitiator	2
Bentonite 27 <sup>f</sup>		0.4
Transparent zinc oxide <sup>g</sup>		3.6

Viscosity @25°C	420 mPa.s
Gloss (60°)	77%
Reactivity (1 lamp 120W/cm)	50 m/min

IVb : does require with Xi and R36/37/38+43

		<u>%</u>
CN104A80 <sup>a</sup>	bisphenol A epoxy acrylate, 80% in TPGDA	48
SR-306 <sup>a</sup>	tripropylene glycol diacrylate (TPGDA)	34.3
SR-9020 <sup>a</sup>	propoxylated glycerol triacrylate (GPTA)	3.2
CN385 <sup>a</sup>	benzophenone	6
NMDEA <sup>h</sup>	N-methyldiethanolamine	2.5
Irgacure 184 <sup>b</sup>	photoinitiator	2
Bentonite 27 <sup>f</sup>		0.4
Transparent zinc oxide <sup>g</sup>		2.6



**436089****Acrylate-functional styrene-allyl alcohol copolymers useful for energy-curable coatings**

Styrene-allyl alcohol (SAA) copolymers are well-known solid, polymeric resins that are useful intermediates for making coatings. The resins have hydroxyl functionality that is stable to acid and bases and can, therefore, be derivatized with carboxylic acids to yield esters. Unsaturated acids (e.g., acrylic, methacrylic, or maleic acid) have been reacted with SAA resins to yield functional oligomers for solvent or liquid-based coatings. For example, U.S. Pat. Nos. 4,017,371, 4,018,940, and 4,045,518 describe the preparation of acrylic esters of SAA to give a solid composition that is crosslinkable with mercaptan-containing compounds. While the references describe the acrylate derivative as a solid, the potential advantages of this feature for solid applications (such as powder coatings) were not pursued. Powder coatings containing UV-curable polymers are known. They are typically based on linear polyester, polyurethane, or epoxy compounds. See, for example, International Publications WO 98/18862, WO 97/44369, WO 99/14254 and European Pat. Appl. No. 0702040.

Esterification of SAA resins can produce a wide variety of combinations of unsaturation, hydroxyl groups, and the possibility of incorporating saturated ester groups. These can be easily modified to give improved adhesion, water repellency, flow and leveling, or reactivity. Hydroxyl functionality on partially esterified SAA resins is also desirable for pigment wetting in curable ink formulations.

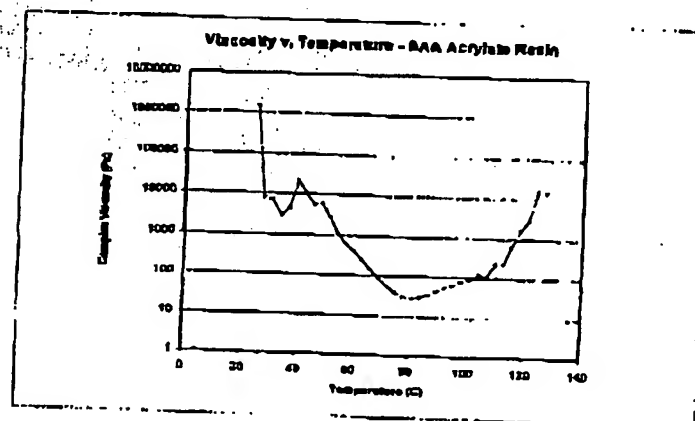
**SAA Acrylate Preparation**

A round-bottom flask is charged with styrene-allyl alcohol copolymer (272 g), toluene (458 g), hypophosphorous acid (38.7 g of 50% aqueous solution), acrylic acid (73.3 g), p-toluenesulfonic acid (17.2 g), and methyl hydroquinone (0.43 g). The mixture is heated to 90°C and is refluxed for 6 h under air sparge with continuous stirring. Water is removed by during the process. The product is cooled for 1 h, and it is then divided into four equal portions. Each part is decanted into a 1-L separatory funnel. To each funnel, an equal amount of hydrocarbon solvent is added. Warm aqueous 30% NaOH solution is added at an amount half that of the reactant weight. The funnel is shaken well, and the phases are allowed to separate for about 2 h. (Note: Phase separation is much faster if tetrahydrofuran, e.g., about 10-30 vol. % based on the amount of

organics, is added to the mixture following base extraction.) The caustic phase is removed, and the extraction process is repeated twice using distilled water. The organic phase is poured into a 1-L round-bottom flask. More methyl hydroquinone (0.05 g) is added, and the product is vacuum distilled at 50°C until the viscosity of the organic layer increases to 1000 to 10,000 centipoise. The product is dried at 55°C under vacuum for about 4 h.

Final resin properties: acrylate content: 2.6 meq/g; hydroxyl number: 37 mg KOH/g; acid number: <1.0 mg KOH/g;  $T_g=43$ ;  $M_n=1700$ . APHA color: 450. (Note that in the absence of an oxidizing acid, the color of the acrylate resin is unacceptable (dark brown). APHA colors can be achieved with at least about 5 wt.%, based on the amount of ester, of hypophosphorous acid; with about 1 wt.%, colors on the Gardner scale are observed.)

The figure below is a melt curve for the SAA acrylate resin. The figure shows that flow occurs below 100°C, making this material useful for powder applications on wood, paper, plastic, and other heat-sensitive substrates. For applications where the resin must be extruded at temperatures above 80-100°C prior to application, the more thermally stable methacrylate esters are recommended to prevent premature crosslinking of the resin.



Disclosed anonymously  
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